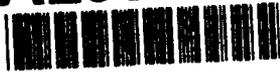


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PRECERAMIC POLYMERS: PAST, PRESENT AND FUTURE

by

Dietmar Seyferth

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PRECERAMIC POLYMERS: PAST, PRESENT AND FUTURE

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ABSTRACT

A review of preceramic polymer chemistry is given. Preceramic polymers are needed because of high technology applications which arose in our aerospace age. A discussion of the early work in Germany and Japan leads to an enumeration of the requirements that must be met if a polymer is to be a useful precursor in pyrolytic ceramic synthesis. Seven current research directions in preceramic polymer chemistry are discussed and the at present uncertain future of preceramic polymer technology is pointed out.

I. INTRODUCTION

A. Why Preceramic Polymers?

Although Aylett (1) and Chantrell and Popper (2) suggested in 1964 that inorganic polymers might serve as precursors for ceramics, active research on inorganic and organometallic polymer pyrolysis as a route to useful non-oxide ceramics began only in the early 1970s. The initiation of inorganic/organometallic preceramic polymer chemistry as a new subarea of polymer science was prompted by the demands of modern high technology, in particular, technology as practised by the defense/aerospace industry. There was a pressing need for new structural materials that could serve as replacements for metals and metallic alloys in many structural applications in advanced aircraft, spacecraft and weapons systems: materials that are as light or lighter than the metal that they replace, that can survive in harsh environments, that have exceptionally high thermal stability (above 1200°C), high strength and fracture toughness, high thermal shock resistance, that are resistant to high temperature air oxidation and to atomic oxygen

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and to chemical corrosion. The outstanding properties of carbon/carbon composites, their superior strength and thermal stability, had already been recognized (3, 4), but, of course, their facile oxidation at higher temperatures in air was a serious flaw. It was expected that replacing the carbon fibers with appropriate ceramic fibers and the carbon matrix with a ceramic matrix would give a composite with greatly superior properties, one that would be stable to high temperature oxidation and that would meet the requirements of the aerospace age (5). This required the availability of a polymer that could be spun into fibers whose subsequent pyrolysis gives the needed ceramic fibers. Because of their superior high temperature properties, silicon carbide (6, 7) and silicon nitride (8,9) were of immediate interest in this application and, as a result, the initial focus was on organosilicon and inorganic silicon polymers. For such polymers, which could serve as useful precursors, through their pyrolysis, to ceramics, the term "preceramic polymers" was applied (10). In this application, the ceramic matrix also could be a product of polymer pyrolysis and the use of ceramic fibers as reinforcing materials in metal, glass and organic polymer matrix composites also is possible.

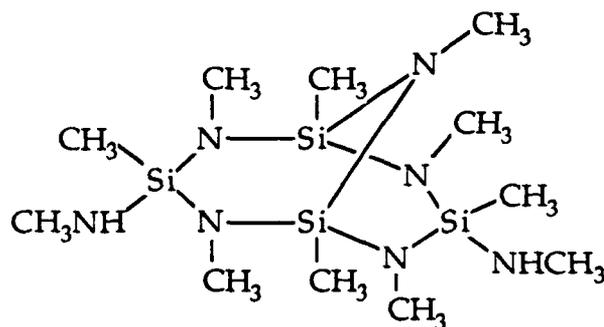
While the use of preceramic polymers in the fabrication of fiber-reinforced composites has aroused the greatest interest, other applications were recognized: as precursors for high temperature oxidation- and corrosion-resistant ceramic coatings for structural parts fabricated from carbon/carbon composites or from reactive metals or metallic alloys; as coatings for carbon and ceramic fibers designed to give the proper fiber/matrix interaction; as low-loss binders for use in conventional fabrication of parts from ceramic powders. In the latter application, the preceramic polymer would replace the organic polymers heretofore used as binders, hopefully resulting in a stronger part that is much freer of defects since the binder would not have to be pyrolyzed out completely, but rather for the most part would be converted to ceramic.

These are just the most obvious applications of preceramic polymers. The fact that they may be processed by conventional polymer processing techniques presents

opportunities for other applications as well: for their use in ceramic/ceramic and ceramic/metal joining, in the preparation of ceramic foams and membranes, to mention just a few.

B. Early Developments.

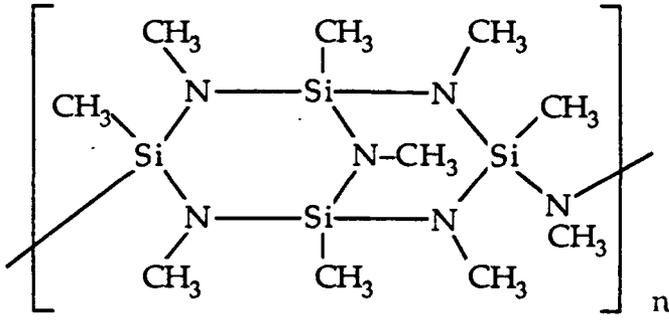
The results of two early research and development efforts, one in Germany, the other in Japan, serve to define the new field of preceramic polymer chemistry. In the laboratories of Bayer AG, Verbeek (11) used the known (12) reaction of methyltrichlorosilane with methylamine to produce $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$. This product had been shown to undergo condensation with loss of methylamine when heated in the presence of H_2SO_4 , giving a bicyclic silazane, **1** (13). Verbeek found that flow thermolysis of $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$ at around 520°C through a Raschig ring-filled glass tube gave volatiles and a brittle, solid "carbosilazane resin" that was soluble in



1

organic solvents. It could be melt-spun at 220°C to give carbosilazane fibers. Before pyrolysis of the green fibers, it was necessary to render them infusible, and this was accomplished by heating them in moist air at 110°C for 20 h. Subsequent pyrolysis in nitrogen to 1500°C gave black, glistening, amorphous ceramic fibers in 45 wt % yield. When they were heated to 1800°C , crystalline material, mostly $\beta\text{-SiC}$ and a little $\alpha\text{-SiC}$ and $\beta\text{-Si}_3\text{N}_4$, was obtained. A detailed study of this carbosilazane preparation and pyrolysis was published by Penn et al. (14). The thermolysis of $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$ appears to form a crosslinked material of higher molecular weight,

and GPC-derived weight average molecular weights of up to 4222 were reported by Penn et al. "Structure" in the classical sense is not meaningful in the case of a preceramic, nonuniformly crosslinked network polymer. At best, the component building blocks can be determined and often quantified by means of the integrated NMR spectra of the polymers. Some local components (e.g., cyclic and linear portions) may be identified. Generally, idealized or composite structures are drawn when the subject of "structure" is discussed. For the $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$ -derived carbosilazane resin the idealized structure 2, in which 1 is the building block, was



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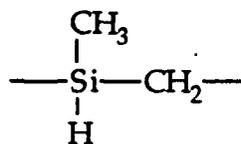
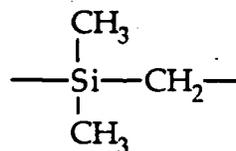
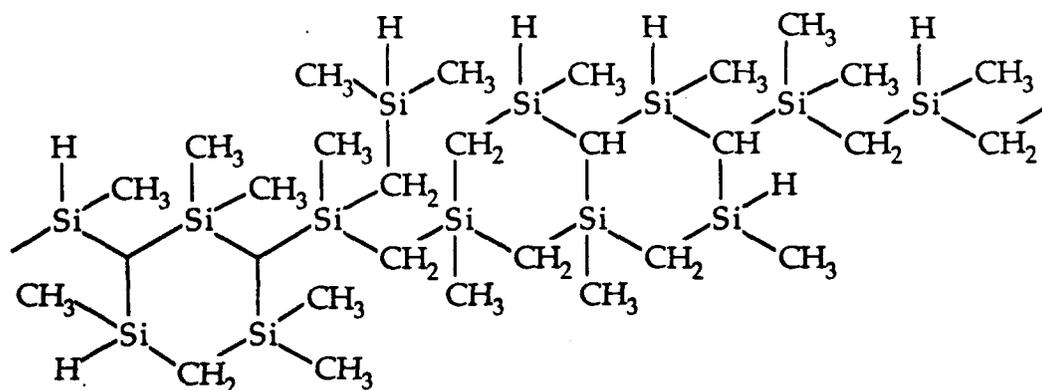
suggested in a review (15). However, the "structure" of the polymer must be more complex than this in view of the well-known thermal lability of the Si-N bond.

In a variation of this procedure, Winter, Verbeek and Mansmann (16) used ammonia in place of methylamine. In this case the product was a poly(methylsilazane) of type $(\text{CH}_3\text{SiN}_{1.5})_n$. (This reaction also had been reported previously (8).) A concentrated solution of the ammonolysis product could be dry-spun (using poly(ethylene oxide) as a spinning aid) to give polysilazane fibers. Their pyrolysis in a stream of nitrogen to 1200°C resulted in silicon carbonitride ceramic fibers. Recourse to the less desirable dry-spinning process was necessary because the polysilazane did not form a stable melt. Ceramic films and shaped ceramic bodies also were made using such polysilazane pyrolysis. These processes never were

commercialized, although, it was reported (15), one of them reached the pilot plant stage.

Verbeek and Winter also developed a preceramic polymer process for silicon carbide (17) based on the prior investigations of Fritz and his coworkers on the thermal decomposition of tetramethylsilane and the methylchlorosilanes (18). Such thermolysis, effected at around 700°C with provision for recycling of starting material, gave a carbosilane resin that could be dry-spun from dichloromethane solution using an organic polymer as spinning aid. Pyrolysis of fibers prepared in this manner to 1500°C in a stream of nitrogen resulted in black ceramic fibers that were amorphous by X-ray diffraction and contained, in addition to SiC, about 10 wt % of free carbon.

Pioneering work on polymeric precursors for silicon carbide was initiated in the early 1970s by the late S. Yajima and his coworkers at the Research Institute for Iron, Steel and Other Metals of Tohoku University in Orai, Japan (19-25). The starting material in this process is the readily available dimethyldichlorosilane. Its reductive dechlorination by sodium, studied earlier by Burkhard at the General Electric Company (26), results in formation of poly(dimethylsilane) (or poly(dimethylsilylene)), $[(\text{CH}_3)_2\text{Si}]_n$, a white, intractable powder. The Japanese workers found that when this material is heated at around 450°C in an autoclave for 14 h (or in the presence of a few wt % of a poly(borodiphenylsiloxane) at 350°C under nitrogen for 10 h), it is converted to a polycarbosilane in which the original Si-Si backbone has been changed to a Si-CH₂ backbone. These polycarbosilanes, as isolated after removal of volatiles, are glassy, resinous materials that are meltable and soluble in organic solvents. They were shown by means of NMR (¹H, ²⁹Si) spectroscopy to contain (CH₃)₂Si and CH₃(H)Si groups bound together by CH₂ and CH bridging units. The major building blocks in these polycarbosilanes are 3 and 4, but the "structure" of these polymers also has been drawn only as an "ideal" one, as shown in 5 (25). They appear to contain both linear and cyclic components and also are nonuniformly crosslinked. They, like the Bayer polysilazanes, are not high

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molecular weight materials ($\bar{M}_n \sim 1250 - 1750$). (This appears to be the case for most organosilicon preceramic polymers.) It was found that the Yajima polymers could be melt-spun at 250 - 350 °C to give "green" polymer fibers. The pyrolysis of these fibers to ceramic fibers required another processing step: they had to be rendered infusible so that the fiber form would be retained when they were pyrolyzed. Such "curing" of the green fibers could be effected by heating them in air between 110 - 190 °C. Pyrolysis in an inert atmosphere at 1200 °C subsequently gave ceramic fibers 10-20 μm in diameter. These, by elemental analysis in one experiment, had the nominal molar composition 1 SiC : 0.78 C : 0.22 SiO₂. These fibers are a commercial product of the Nippon Carbon Company and are sold under the trade name Nicalon. They have excellent properties at temperatures up to about 1200 °C: tensile strengths of 2500 - 3200 MPa, Young's modulus of 180-200 GPa, acid and base corrosion resistance and resistance to oxidation. However, above 1200 °C, SiC crystallization and grain growth occur and solid state reactions between the SiO₂ formed in the cure step and elemental carbon and SiC generate CO and SiO, both

gases whose evolution in the interior causes significant damage. As a result, the mechanical strength of the fibers is lost.

A variation of the Nicalon polycarbosilane process was developed by Yajima and his coworkers. Heating a xylene solution of the polycarbosilane obtained by the route in which the poly(borodiphenylsiloxane) was used as catalyst with $(n-C_4H_9O)_4Ti$ (10 : 7 weight ratio) at 130°C for 1 h, removal of solvent and heating of the residue at 220°C for 30 min gave a new titanium-containing, soluble, more highly crosslinked polymer (27). Pyrolysis of this material in an inert gas stream to 1200°C gave an amorphous Si, Ti, C and O-containing ceramic. Heating this material to 1700°C caused crystallization of β -SiC and TiC phases. The ceramic yield, as expected, was higher (>70% vs ~60%) than that obtained with the polycarbosilane that had not been crosslinked with the titanium alkoxide. Continuous Si/Ti/C/O-containing ceramic fibers could be prepared from this polymer (28). These are made and marketed by Ube Industries Ltd. under the trade name Tyranno. A Young's modulus of 220 GPa was reported for these fibers. Their high temperature strength was found to be superior to that of Nicalon fibers.

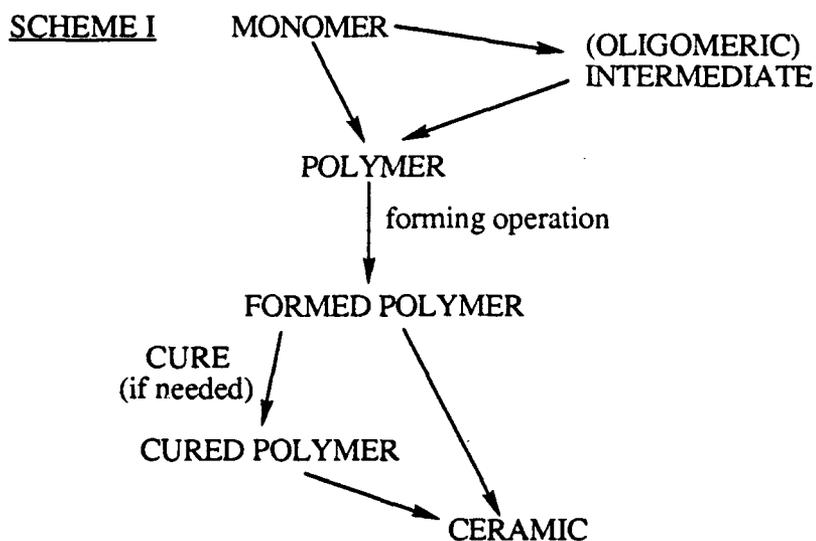
II. REQUIREMENTS FOR A USEFUL PRECERAMIC POLYMER.

This brief discussion of the early preceramic polymer systems makes obvious some of the requirements that are important for the preparation of a useful preceramic polymer. These requirements are dictated by the intended application of the preceramic polymer and can vary from application to application. For instance, its use in the fabrication of ceramic fibers will require different properties than when its intended use is as a binder in ceramic powder processing. Thus the preceramic polymer must be "tailor-made" for successful use in the intended application. This requires close collaboration between the synthetic chemist, the ceramist, and the end-user. Successful preceramic polymer technology is an interdisciplinary effort.

Some general principles have been recognized as the field of preceramic polymer chemistry has developed. Although at the present time the aerospace

industry is by far the major end-user of preceramic polymer-derived products, one would hope that the technology based on this new approach will penetrate far broader markets, especially those in the civilian sector, for instance, the automobile industry. Thus cost factors are important and critical non-technical requirements are that the starting material be reasonably cheap and readily available and that the synthesis of the preceramic polymer be as uncomplicated as possible in terms of processing. In the two examples cited above, the starting materials both are products of the reaction of methyl chloride with Si/Cu (Rochow/Müller Direct Synthesis), which produces methylchlorosilanes (mainly $(\text{CH}_3)_2\text{SiCl}_2$, but also CH_3SiCl_3 , $\text{CH}_3\text{SiHCl}_2$ and $(\text{CH}_3)_3\text{SiCl}$ as by-products) which are the foundation of the worldwide silicones industry. Thus both are readily available and not expensive. In either case, however, the chemical processing is not as simple as one would like to have it.

The steps involved in the preceramic polymer technology, starting with the monomer and ending with the ceramic, are shown in Scheme I. In the preparation



of inorganic and organometallic polymers, the condensation processes involving the monomer often give oligomeric, usually cyclic products. These then must, in one way or another, be converted to materials of higher molecular weight. In

organic polymer technology, the final major step is the forming operation. In preceramic polymer chemistry, the shaped polymer (fiber, coating, matrix in a composite, binder in powder-derived part) must be pyrolyzed to the final ceramic. If the shape is to be retained (e.g., the fiber form), then the polymer must be infusible or rendered infusible or it will melt with loss of its shape. In the case of melt-spun fibers, a "cure" step is required, as has been noted in the discussion of both the Bayer carbosilazane resin and the Nicalon polycarbosilane. However, many preceramic polymers are "self-curing", i.e., they become infusible during the early stages of the pyrolysis without going through a melt stage and thus the shape is retained.

If a preceramic polymer is to be a useful one, first and foremost, it must be processable by conventional polymer processing techniques. For most applications it must be soluble, preferably in common organic solvents. If it is a solid, it should be fusible, forming a stable melt, if ceramic fibers are the goal, i.e., it should be melt-spinnable. (Melt-spinning is preferable to dry-spinning: no solvent is required and, in general, the resulting green fibers have better properties.) A solid polymer is not always necessary or desirable. For other applications, oligomeric fluids of various viscosities are required.

The preceramic polymer should be stable at room temperature. Specifically, it should not undergo further crosslinking on storage that could lead to decreased solubility or even insolubility. It would help if it were stable to atmospheric moisture and oxygen, but that is not always possible (e.g., the example of the polysilazanes which are more or less readily hydrolyzed on exposure to air).

Another important requirement is that pyrolysis of the inorganic or organometallic preceramic polymer give as high a yield of ceramic residue as possible. Ceramic yields ($= \text{weight of ceramic residue} \times 100 / \text{weight of pyrolysis charge}$) of 60-75% are acceptable, but higher ceramic yields of 80% or greater are desirable. Most polymers that have an inorganic backbone contain substituents on some or all of the backbone atoms. These often are hydrogen atoms or organic

groups, but they can be of other types. During the pyrolysis of the polymer these substituents may become incorporated into the ceramic residue or they may be eliminated in the form of volatile, low molecular weight compounds that escape as gaseous products at the high pyrolysis temperatures. Thus H and CH₃ are preferred substituents since their loss will leave a high ceramic residue yield (if the backbone atoms are retained). The pyrolysis of a polymer may give the theoretical yield of a ceramic as represented by the backbone atoms, but if the ceramic yield is low because of the large contributing weight to the pyrolysis charge of rather heavy substituents that will end up as volatiles, then useful applications of the polymer may be questionable. The high ceramic residue yield is of importance not from economic considerations. Rather, a high ceramic yield means that the quantity of gases evolved during pyrolysis will be small. These gases can be very destructive, especially if they are released over a narrow temperature range, causing cracking or even rupture of the ceramic part. So the fewer evolved gases, the better from the point of view of "good" ceramics. Lower ceramic yields, however, can be tolerated if the porosity generated in the developing ceramic during the pyrolysis is of the right kind: open porosity that lets the pyrolysis gases escape. Also, the greater the weight loss of a preceramic polymer on pyrolysis, the greater will be the shrinkage of the residual body. However, shrinkage is unavoidable when a polymer is pyrolyzed to a ceramic since one is starting out with a material of low (1 g/cc or less) density and is forming a material of greater (2-3 g/cc) density.

The requirement of high ceramic yield on pyrolysis determines the nature of the polymer that will be satisfactory. Ideally, the polymer should already be crosslinked (but not to the point of insolubility). More importantly, whether crosslinked or not, it should undergo extensive crosslinking during the early stages of the pyrolysis so that evolution of volatiles is minimized and the elements of interest are retained in the hot zone. To accomplish this, the polymer must contain reactive functionality ("latent functionality" in the words of Wynne and Rice (10)) that on heating will react rapidly to cause the needed further crosslinking. The

design of a useful preceramic polymer thus requires the introduction of reactive functional groups in the monomer and/or, later, in the polymer so that the initial stage of the pyrolysis results in formation of a highly crosslinked, nonvolatile, probably insoluble network, hence in a high ceramic residue yield.

Another important requirement is that the polymer have the right rheological properties for the intended application. This is an important consideration when melt-spinnable fibers are desired, when thick or thin film coatings are to be prepared and when the preceramic polymer is to be used as a binder for ceramic powder formulations for injection or compression molding. In this connection, the ability to control the molecular weight of the polymer is important. A given molecular weight range will give rheological properties that may be satisfactory for one application but not for another.

Since this early work by Verbeek and Yajima and their respective coworkers, the field of preceramic polymer chemistry has become a very active one, with participation by scientists in industrial, academic and government laboratories throughout the world. The field has advanced considerably during the past twenty years. Research and development efforts have been directed in the main at the synthesis of polymeric precursors for silicon-containing ceramics: silicon carbide, silicon nitride and silicon carbonitride, but precursors for boron nitride and carbide, aluminum nitride and early transition metal carbides and nitrides also have been of interest. Numerous reviews covering this work have been published (10, 15, 25, 29-38). Rather than summarizing this work, it may be more useful to point out and discuss briefly some of the current research directions in the preceramic polymer area.

III. CURRENT RESEARCH DIRECTIONS IN THE PRECERAMIC POLYMER AREA

A. Single Phase Ceramics via Polymer Pyrolysis.

Much effort still is devoted to synthesis. Until recently, the preparation of pure (i.e., single phase) ceramics by polymer pyrolysis has not been straightforward and

the tendency has been to take what you get in the pyrolysis of a given polymer. "What you get" is not always optimum in terms of ceramic composition and may even be rather unsatisfactory. A surprising amount of effort still is devoted to the synthesis and study of preceramic polymers that clearly are impractical with respect to eventual commercialization in terms of expense, unavailability or instability of the starting material used, expense or complexity of the chemical processing, properties of the polymer prepared or the properties and composition of the ceramic formed on pyrolysis of the polymer.

There are, however, more and more synthetic efforts aimed at preparation of preceramic polymer systems where "what you get" on pyrolysis is really what you want or need. Some of these efforts are directed at the preparation of polymeric precursor systems whose pyrolysis will give single-phase ceramic products. There are several ways of accomplishing this, as will be described below. However, this does not mean that ceramic products consisting of more than one phase are not useful. Quite the contrary: mixed phases are of some interest and utility and we shall return to this point later on.

In the case of pure, non-oxide silicon ceramics, the target ceramics are silicon carbide, SiC, and silicon nitride, Si₃N₄. However, in most cases, pyrolysis of a preceramic organosilicon polymer does not give anything approaching these pure ceramic phases. In most organosilicon polymers (e.g., the Nicalon polycarbosilane), the C:Si ratio is greater than 1. However, in the case of the preparation of SiC by polymer pyrolysis, one would like to achieve a 1:1 C:Si ratio in the ceramic or, at the most, SiC plus only a small amount of free carbon, since carbon is a sintering aid for SiC. With most preceramic organosilicon polymers, a substantial amount of free carbon remains in the final ceramic product after pyrolysis. At the least, a large amount of free carbon in the ceramic product will bring problems of high temperature oxidation. If there also is oxygen in the ceramic, introduced in the synthesis of the polymer or in its subsequent processing, the high temperature reactions with free carbon that generate gaseous CO cause serious problems. On the

other hand, an organosilicon polymer whose pyrolysis results in formation of substantial amounts of elemental silicon in addition to SiC also is unsatisfactory. Such free silicon (mp 1414°C) would compromise the high temperature applications of the ceramic part.

A 1:1 C:Si ratio in the preceramic polymer does not guarantee that stoichiometric SiC will be produced in its pyrolysis since the pyrolysis chemistry might be such that one of these elements will be lost in part in the form of gaseous products. Polymer composition and pyrolysis chemistry both are important. A notable example of a polymer in which the C:Si ratio is one and in which the pyrolysis in a stream of nitrogen gives essentially pure SiC in high yield is the polycarbosilane $[\text{H}_2\text{SiCH}_2]_n$ (39). On the other hand, pyrolysis in a stream of argon of the poly(methylsilane) $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$ ($x + y + z = 1$; $x \gg y, z$), which also has a C:Si ratio of one, evolved substantial amounts of CH_4 and left, in low yield, a ceramic residue composed of 76 wt % SiC and 24 wt % elemental silicon (40). However, further chemical manipulation of this system was possible, and we found that heating this poly(methylsilane) in hexane with 0.5 mol % (based on Si) of $[(\eta^5\text{-C}_5\text{H}_5\text{ZrH}_2)]_n$ or $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$ resulted in a crosslinked polymer whose pyrolysis gave near-stoichiometric SiC in high ceramic yield (41). In one example, use of the zirconium hydride catalyst gave as final nominal ceramic composition 98 wt % SiC, 1.6 wt % ZrC and 0.4% Si. Since the poly(methylsilane) was prepared by the simply effected reaction of sodium with $\text{CH}_3\text{SiHCl}_2$, this represents an economical route to SiC. The catalytic crosslinking chemistry is based on Harrod's Ti or Zr complex-catalyzed dehydrogenative coupling of primary silanes, RSiH_3 , to give oligomeric polysilanes (42).

Silicon nitride of good purity is accessible by pyrolysis in a stream of ammonia of the complex perhydropolysilazane prepared by ammonolysis of the H_2SiCl_2 -pyridine adduct in pyridine solution (43, 44; see also 45). The 1:1 Si:N ratio in the polysilazane should lead to a ceramic product containing an excess of elemental Si and does indeed do so when the pyrolysis is carried out in an inert gas stream.

However, when the pyrolysis is carried out in a stream of ammonia, reaction of NH_3 , or of N_2 formed in its decomposition, with the elemental silicon converts this to Si_3N_4 , so that a pure ceramic product is obtained.

This example illustrates the importance of the gas stream used in the pyrolysis of a preceramic polymer. Polymer pyrolysis usually is carried out in a furnace through which a gas is flowing. The gas stream serves two purposes: to protect the system from the atmosphere and to sweep away the volatiles produced in the pyrolysis. The gas used may be either an "inert" gas or a "reactive" gas. The pyrolysis of our polysilazane of composition $[(\text{CH}_3\text{Si}(\text{H})\text{NH})_a(\text{CH}_3\text{SiN})_b]_n$ (46-48) serves to illustrate the use of both types of pyrolysis gas stream. Pyrolysis of this polysilazane in a stream of argon (an inert gas) to 1000°C gives a black ceramic residue in 80-85% yield. This material is amorphous, so composition in terms of pure species such as SiC and Si_3N_4 is meaningless. However, the analytical results (%C, N, Si) can be used to calculate a hypothetical composition in terms of SiC , Si_3N_4 and free C. The results of such a calculation in one case were: 67% by weight of Si_3N_4 , 28% SiC and 5% C. This may be close to the actual composition of this material when it becomes crystalline above 1450°C . In marked contrast, when this polysilazane is pyrolyzed to 1000°C in a stream of ammonia, a white solid residue is obtained. This usually contains less than 0.5% by weight of carbon and is almost pure silicon nitride. The chemistry that takes place at temperatures of $400\text{-}600^\circ\text{C}$ to remove the carbon must be complex. Nucleophilic cleavage of methyl groups from silicon by NH_3 to give CH_4 and generate Si-NH_2 functions may be involved at the lower temperatures, but at high temperatures NH_2 and NH radicals derived from NH_3 may be the reactive species. Such pyrolysis in a stream of ammonia serves also to remove diamine ligands from $[\text{B}_{10}\text{H}_{12}\cdot\text{diamine}]_n$ polymers, giving BN as the final ceramic product (49) and to remove organoamino substituents from titanium in $(\text{Me}_2\text{N})_2\text{Ti}[(\text{RNH})_2\text{Ti}]_x(\text{NMe}_2)_2$ polymers, giving TiN (50). It is noteworthy that pyrolysis of a polycarbosilane that contains no Si-N bonds at all gives silicon nitride as the ceramic product when effected in a stream of ammonia. For example, such

NH_3 pyrolysis of the Nicalon polycarbosilane has been reported to produce Si_3N_4 (51). Thus, what we refer to as the "carbon kickout" reaction appears to be generally applicable in the preparation of nitride ceramics.

A single monomer is not necessarily required in order to obtain near-stoichiometric SiC. One may make use of the fact that elemental carbon and silicon react to give SiC, especially so if they are generated *in situ* as finely dispersed pyrolysis products. As mentioned above, most organosilicon polymers when pyrolyzed in argon give SiC plus an excess of free carbon and, on the other hand, pyrolysis of our $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$ poly(methylsilane) gives SiC plus an excess of free silicon. Thus if we take our "silicon-rich" poly(methylsilane) and a "carbon-rich" organosilicon polymer in the appropriate quantities, either in chemical or physical combination, the excesses of Si and C react and close to stoichiometric SiC is obtained in the pyrolysis. One cannot always predict what the elemental composition of the derived ceramic obtained on pyrolysis of a preceramic polymer or a mixture of preceramic polymers will be, so for the most part it is a matter of doing experiments until pyrolysis trends are recognized. This empirical approach does, however, work. An example of a chemical combination of poly(methylsilane) and a "carbon-rich" organosilicon polymer is the hydrosilylation reaction product of $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$ with the poly(silaacetylide) $[(\text{CH}_3(\text{CH}_2=\text{CH})\text{SiC}\equiv\text{C})_n$ (52). An AIBN-catalyzed reaction (Si-H to CH=CH addition) between appropriate quantities of these two polymers gave a hybrid polymer whose pyrolysis in a stream of argon resulted in formation of SiC, 99% pure by elemental analysis. An example of a physical combination whose pyrolysis gave near-stoichiometric SiC is the appropriate mixture of the poly(methylsilane) and the Nicalon polycarbosilane.

B. Multiphase Ceramics via Polymer Pyrolysis.

As noted above, a mixture of different ceramic phases may be a useful product because of its superior properties compared with those of the pure components. A

striking example is that of composites of SiC and TiC which have greater fracture toughness (maximum at a 50:50 wt % mixture) than pure SiC and TiC (53). Such a composite was prepared earlier by Yajima and his coworkers (27), as noted above in this discussion. At M.I.T. we have prepared polymeric precursors for SiC/MC (M = Ti, Zr, Hf) composites by UV-induced reaction of the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$ poly(methylsilane) with stoichiometric quantities of the respective $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CH}_3)_2$ compounds (54). The SiC/MC ceramic product obtained in their pyrolysis in a stream of argon contained significant amounts of free carbon (up to 40 wt % in the case of M = Ti). This could be avoided by pyrolyzing a composite of the Si- and M-containing polymer with the respective M metal powder. A low-carbon SiC/MC composite resulted on high temperature reaction of the free carbon formed in the pyrolysis with the M metal powder.

In the case of the SiC/MC composites, the ceramic products were heated sufficiently high and long to cause crystallization of β -SiC and MC. However, crystalline ceramic products are not always desirable, and there is reason to believe that amorphous ceramic products in which grain growth cannot occur are advantageous in some applications. Thus the amorphous, covalent silicon carbonitrides obtained by pyrolysis in an inert gas stream of diverse poly(organosilazanes) to around 1200-1300°C appear to be a quite acceptable for many applications.

We also have prepared polymeric silazanylborazines by reaction of the cyclic $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$ oligomers obtained by ammonolysis of $\text{CH}_3\text{SiHCl}_2$ with a BH_3 -Lewis base adduct such as $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ and $\text{H}_3\text{B}\cdot(\text{CH}_3)_2\text{NH}$ (55). Their pyrolysis in a stream of ammonia gave amorphous borosilicon nitrides in high ceramic yield. This work was prompted by reports that $\text{Si}_3\text{N}_4/\text{BN}$ composites had, in some respects, properties superior to those of pure Si_3N_4 and BN (56-59). Also of interest is the preparation by Interrante and his coworkers of various mixed ceramics (Si/AlN, $\text{Si}_3\text{N}_4/\text{AlN}$, $\text{Si}_3\text{N}_4/\text{BN}$, AlN/BN and TiN/BN) by the polymer pyrolysis route (60-62). It may be expected that the preparation of such ceramic/ceramic

composites will become an active research direction in preceramic polymer chemistry.

C. The Problem of Shrinkage in Polymer Pyrolysis.

In general, shaped ceramic parts are not fabricated by pyrolysis of a preceramic polymer alone because, as noted earlier, the shrinkage is enormous on going from the green polymer part to the final ceramic part. Furthermore, the ceramic part thus obtained is very porous and far from theoretical density, hence is not very strong. Instead, the preceramic polymer is used as a low-loss binder for ceramic powders in the fabrication of parts by compression or injection molding with subsequent (usually pressureless) sintering. Such parts, despite the fact that they contain significant porosity and are not fully dense, can be quite strong. In pioneering work, Semen and Loop at the Ethyl Corporation laboratories have demonstrated strengths of over 650 MPa for parts made from submicron SiC particles bonded with an amorphous silicon carbonitride matrix generated by pyrolysis of a polysilazane of type $[(\text{CH}_3\text{Si}(\text{H})\text{NH})_a(\text{CH}_3\text{SiN})_b]_n$ (63). Additionally, these parts were found to exhibit excellent oxidation resistance and strength retention at temperatures up to 1300°C. The overall porosity in these parts was 20-25%; however, the porosity in the matrix is closer to 50% since the SiC particles were fully dense. These results clearly demonstrate the feasibility of achieving superior properties in porous, polymer-derived ceramics. On the other hand, Riedel et al. (64) have prepared a Si_3N_4 composite containing 24 wt % SiC particulates by sintering in nitrogen to 1750°C (with Al_2O_3 and Y_2O_3 as sintering aids) an amorphous silicon carbonitride powder obtained by pyrolysis of a Chisso Corp. polysilazane in an inert gas stream. A ceramic part with 97% relative density that had fracture strength and toughness similar to those of conventionally processed SiC/ Si_3N_4 composites was obtained. A special advantage of this approach was an observed better reproducibility of these properties due to improved homogeneity in the microstructure of the part. A

disadvantage, which can be decisive with respect to possible commercial application, is that using 100% polymer will (at least at the present time) be very expensive.

The problem of shrinkage when a preceramic polymer alone, or even a preceramic polymer/ceramic powder composite, is pyrolyzed has been addressed by Greil and Seibold (65, 66). In a new approach that they call "active filler-controlled pyrolysis", a commercial polysilsesquioxane, $[\text{RSiO}_{1.5}]_n$ (R mostly Ph; minor contents (for thermal crosslinking) of R = H, $\text{CH}_2=\text{CH}$ and CH_3)/Ti powder composite was pyrolyzed in a stream of argon to 1400°C . Titanium carbide was formed by reaction of the titanium powder with carbon from the decomposition products of the polymer, so that the final ceramic was comprised of TiC particles dispersed in a microcrystalline silicon oxycarbide matrix (β -SiC, SiO_2 and graphitic C). This procedure results in very significantly less shrinkage in formation of the final ceramic part in comparison with that observed when the filler-free polymer is pyrolyzed and it may find useful application in the preparation of ceramic parts by polymer pyrolysis. In independent studies at M.I.T., with different intentions, we have used pyrolysis of organosilicon preceramic polymer/metal powder composites in argon to generate ceramic/ceramic composites such as SiC/TiC, SiC/ZrC, SiC/TaC, SiC/NbC, SiC/TiN, SiC/ZrN, as well as transition metal silicides such as W_5Si_3 , Mo_5Si_3 , WSi_2 , MoSi_2 and Mo_3Si (Tables I-III) (67). The polymers used included the Nicalon polycarbosilane, the M.I.T. $[(\text{CH}_3\text{Si}(\text{H})\text{NH})_a(\text{CH}_3\text{SiN})_b]_n$ polysilazane and the M.I.T. $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$ poly(methylsilane). Different phases were obtained when the initial pyrolysis was carried out in ammonia to 800°C before continuing to 1500°C in argon. This approach could be extended to the preparation of ceramic/ceramic composites containing transition metal borides (e.g., TiB_2 , HfB_2 , CrB , CrB_2 , MoB , Mo_2B , WB , W_2B and LaB_6) using the $[\text{B}_{10}\text{H}_{12} \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_n$ polymer as the boron source (67).

Table I. Crystalline Phases from Metal Powder-Polysilazane Composites Pyrolyzed to 1500° C Under a Flow of Argon.

Metal	M : Si	Ceramic yield (%)	XRD results
Ti	1.2 : 1	72	TiN + SiC
Zr	1.3 : 1	82	ZrN + SiC
V	1 : 1	54	V ₅ Si ₃ + SiC
Nb	1 : 1	80	NbC + NbSi ₂
Mo	1 : 2	73	MoSi ₂ + Mo ₅ Si ₃
Mo	1 : 1	80	Mo ₅ Si ₃
W	1 : 1	87	WC + WSi ₂ + W ₅ Si ₃ + SiC
W	5 : 3	93	WC + W ₅ Si ₃

Table II. Crystalline Phases from Metal Powder-Polysilazane Composites Pyrolyzed at 800° C for 4h Under Ammonia Flow, then at 1500° C Under a Flow of Argon.

Metal	M : Si	Ceramic yield (%)	XRD results
V	1 : 1	49	V ₂ N + V ₅ Si ₃
Mo	1 : 1	73	Mo ₅ Si ₃
W	1 : 2	76	W ₅ Si ₃ + WSi ₂
W	5 : 3	89	W ₅ Si ₃ *

* Anal.: W, 93.32; Si, 4.42; C, N, <5.

Table III. Crystalline Phases from Metal Powder-Nicalon PCS Composites Pyrolyzed to 1500° C Under a Flow of Argon.

Metal	M : Si	Ceramic yield (%)	XRD results
Mo	1 : 1	91	α-Mo ₂ C + Mo ₅ Si ₃ + SiC
W	1 : 2	85	WC + WSi ₂ + SiC *
Ti	1 : 1	80	TiC + SiC
Zr	1 : 1	87	ZrC + SiC
V	1 : 1	79	V ₈ C ₇ + SiC
Nb	1 : 1	85	NbC + SiC
Ta	1 : 1	83	TaC + SiC

* Anal.: W, 68.73; Si, 16.77; C, 10.80 (equiv. to ~ 0.38 WC, 0.59 SiC, 0.03 WSi₂)

D. Laser Pyrolysis of Oligomer Aerosols.

In an interesting application of preceramic polymer chemistry, Gonsalves and his coworkers have prepared nanophase ceramic particles by pyrolysis of an aerosol of a liquid mixture of oligomeric cyclosilazanes, $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$ (obtained by ammonolysis of $\text{CH}_3\text{SiHCl}_2$) in a laser plume (68, 69). As shown in Fig. 1, the silazane precursor is injected into the plume of a high power CO_2 laser using an ultrasonic nozzle to generate the aerosol. Important features of this process are the

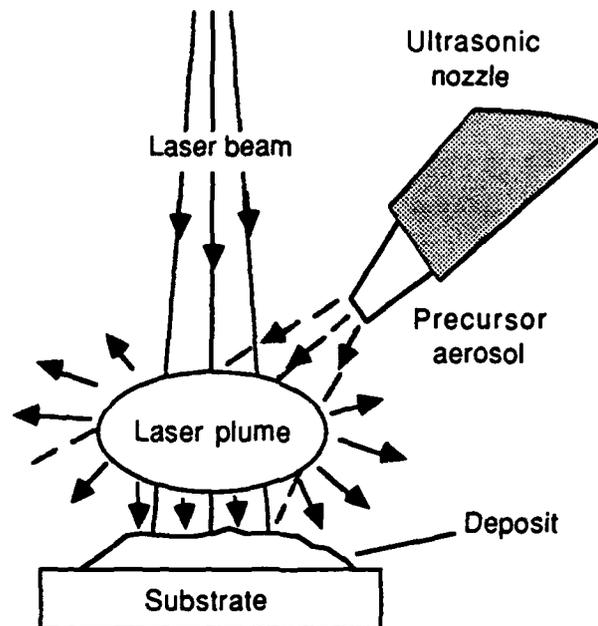


Fig. 1 Technique to form ceramic coatings by rapid condensation of fine particles from laser plume onto laser-heated substrate. (from *Chem. Eng. News*, Sept. 10, 1990 issue, p. 23)

three-dimensional crosslinking and polycondensation reactions that result in ultra-rapid condensation of molecular species from the laser plume. The nanosized silicon carbonitride particles that are produced can be rapidly condensed onto a laser-heated substrate and sintered to form a deposited layer (Fig. 1). In an alternate configuration, the nanoparticles of the ceramic may be collected for processing into bulk material. This process is capable of being scaled up and has great promise for the preparation of ceramic coatings and parts.

E. Ceramic Fibers via Polymer Pyrolysis.

The research direction with which preceramic polymer chemistry first started, the preparation of continuous ceramic fibers, also is a current research direction and no doubt still will be one in the future. The fabrication of ceramic fibers that are useful at high temperatures from a preceramic polymer is the most challenging and difficult task in the preceramic polymer field. The best organic fibers are prepared from linear, high molecular weight polymers. However, polymers of this type, in general, are not useful ceramic precursors since they fragment into volatile products, either starting monomer or cyclic oligomers, when pyrolyzed, leaving little or no solid residue. The good preceramic polymers that have been prepared to date are crosslinked, network-type polymers, generally of low molecular weight ($\bar{M}_n \sim 500-3000$). They can be converted to fibers only with difficulty and the green fibers that result are rather fragile. Their conversion to ceramic fibers also is fraught with difficulties. If melt-spun, they must be cured prior to pyrolysis, and if the cure chemistry involves hydrolysis or oxidation, oxygen is introduced into the ceramic. As noted in the case of the Nicalon fibers, the oxygen content causes fatal problems at high temperatures. Today, almost twenty years since Yajima's original research, the Nicalon fibers of the Nippon Carbon Co. still are the only preceramic polymer-derived ceramic fibers that are commercially available in greater than developmental quantities. Other companies have silicon carbide-, silicon nitride- or silicon carbonitride-based fibers under development, but their future is as yet uncertain. It is, perhaps, ironic that one of the recommendations of a study of the U.S. high performance fiber industry by the National Materials Advisory Board, *published this year*, was that research on ceramic fibers should be undertaken to develop fibers with enhanced stability for use at temperatures above 1200°C. Exactly the same recommendation was being made more than ten years ago!

Since oxidative and hydrolytic cures of melt-spun fibers bring major problems when the ceramic fiber produced is heated to high temperatures, alternative cures

have been examined in more recent work. For example, the Dow Corning HPZ polysilazane fiber precursor, of gross composition $[(\text{SiH}_{39.7})(\text{Me}_3\text{Si})_{24.2}(\text{NH})_{37.3}(\text{N})_{22.6}]$, is cured by exposure to a trichlorosilane, RSiCl_3 (preferably $\text{R} = \text{H}$). This results in a chemical reaction in which Me_3SiCl is eliminated and further crosslinking takes place (70). Alternatively, radiation curing of the green fiber is possible. Electron beam or γ -irradiation of uncured Nicalon polycarbosilane fibers of very low oxygen content effected the required cure. The resulting, essentially oxygen-free, ceramic fibers had much greater tensile strength and Young's modulus compared to those of fibers which had been subjected to the usual air cure (71, 72). This very promising approach is receiving current attention in Japan.

A completely different approach to spinning of SiC fibers that also uses preceramic polymer is the "slurry spinning" method developed by workers at du Pont (73). In this procedure, an ultrasonicated slurry containing α - or β -SiC, B_4C as sintering aid, a dispersant, and 18.5% by wt of Nicalon polycarbosilane (as a binder) in xylene was evaporated to a "toothpaste consistency", homogenized and then "spun" by extrusion through 4 mil holes and attenuated to a final diameter of 50 μm . Pyrolysis in argon then gave SiC fibers of ca 30 μm diameter that retain their room temperature properties after being heated for 120 h at 1500°C at room temperature. Apparently, with such SiC/polycarbosilane systems a cure step is not necessary.

F. Ceramics Containing Heteroelements Other Than Silicon via Polymer Pyrolysis.

Most of this discussion has focused on silicon-based preceramic polymers. However, other ceramics have some of the superior properties of the type that materials scientists are seeking: boron nitride and carbide, aluminum nitride (more of interest for electronic applications), the early transition metal carbides, nitrides, borides and silicides, and there is growing research activity directed toward useful polymeric precursors for these materials. Precursors for boron nitride have received the greatest attention, with most work devoted to borazine-derived polymers

(reviewed in (74)). However, higher boron hydrides also have served as the boron source in polymeric precursors for BN. Thus pyrolysis of poly(2-vinylpentaborane(9)) in a stream of ammonia to 1000°C gave BN in high yield (75). Mentioned earlier was a similar ammonia pyrolysis of $[B_{10}H_{12} \cdot \text{diamine}]_n$ polymers which also gave BN in high yield (49). Pyrolysis of poly(2-vinylpentaborane(9)) in argon to 1000°C resulted in formation of boron carbide in high yield (76).

A melt-spinnable, thermoplastic polymer of composition $[(EtAlNH)_a \cdot (Et_2AlNH_2)_b \cdot (AlEt_3)_c]_n$ ($a + b/c \sim 50$) was prepared by Bolt and Tebbe (77-79) by reaction of triethylaluminum with ammonia. Aluminum nitride fibers could be prepared by melt-spinning the polymer and pyrolyzing initially in ammonia and, at higher temperatures, in nitrogen. Heating to 1600-1800°C resulted in formation of polycrystalline AlN.

A novel electrochemical preparation of a polymeric precursor for aluminum nitride was reported by German workers (80, 81). In this process, metallic aluminum was dissolved anodically in a mixture of a primary amine and acetonitrile that contained a tetraalkylammonium salt as the supporting electrolyte. A polymeric iminoalane gel was formed on removing the solvent and heating the residue to 150°C. Pyrolysis to 1100°C in ammonia removed RN substituents, giving crystalline AlN. Such electrochemically-generated precursor solutions could be used to prepare AlN coatings on SiC fibers (82). The same type of poly(iminoalane) precursor, $[HAlNPr-i]_6$, was prepared by reaction of isopropylamine with $LiAlH_4$ in refluxing heptane (83). Pyrolysis to 1000°C in argon gave an amorphous, Al- and N-containing ceramic. Heating of this material to 1600°C caused crystallization of AlN.

G. Investigation of the Polymer Pyrolysis Process.

Also to be noted among the current research directions in preceramic polymer chemistry are the many studies aimed at gaining a better understanding of the polymer pyrolysis process and of the ceramic that is formed. Techniques such as

TGA/GC/MS and TGA/GC/FTIR have been found useful in the study of the evolution of volatile products in the pyrolysis as a function of temperature. Solid state NMR spectroscopy (^{29}Si , ^{11}B , ^{13}C , ^1H , ^{27}Al , etc.) and diffuse reflectance FTIR spectroscopy have been used to study the developing amorphous solid pyrolysis residue, and powder X-ray diffraction to study the developing crystalline phases that are formed at higher temperatures. From such studies (which by now are too numerous to cite), a good picture of the pyrolysis chemistry of the organosilicon preceramic polymers is emerging. Also being carried out in various laboratories are detailed studies of the microstructure development as a function of the starting polymer and the pyrolysis process variables. Although finding and developing new directions in preceramic polymer chemistry and technology is an exciting and rewarding activity, understanding what has been done also is of great importance. This understanding is vital to the further progress of the field.

IV. THE FUTURE OF PRECERAMIC POLYMER CHEMISTRY?

These then are some of the current research directions. But where, one might ask, is the field of preceramic polymer chemistry and technology heading? Indeed, is it a viable field that has a future? The answer to these questions is not at all clear at the present time.

As noted already, preceramic polymer chemistry is an area of applied polymer science/ceramic science. It is market-driven: the end-goal is a product. Preceramic polymer chemistry has been supported in the research laboratory and developed by industry because there were important potential commercial applications in sight. In the middle-to-late 80s there was general enthusiasm for and ever-increasing R&D activity in this new field of polymer science and, more generally, in advanced ceramics, first in Japan, then in the USA, more recently in Europe. In the meantime, the picture has changed. Most of the immediate applications of preceramic polymers mentioned earlier in this article were in the area of aerospace, and a large fraction of the R&D activities in the USA received its major support

from DOD, DOE and NASA. In the time of big defense budgets that supported the development of evermore sophisticated and demanding (in terms of stresses to be tolerated) jet aircraft, space vehicles, missiles, etc., the future of advanced structural ceramics, and thus of the preceramic polymer field, seemed secure. Preceramic polymers were urgently needed and the activity in the field – chemistry and ceramics – grew rapidly, with many chemical companies initiating research in this new area. Now, however, defense budgets worldwide are getting smaller. Budget deficits lead to reductions in space-related activities. The National Aerospace Plane, to which much of the advanced structural ceramics technology would be applied, is in jeopardy. In short, the perceived market for preceramic polymers is shrinking. Add to this the fact that the time required for development of a final product in the preceramic polymer technology area has turned out to be much longer than had been expected, so that R&D costs are very high. As a result, those companies whose vision is restricted to short-to-moderate term profitability that had ventured into the preceramic polymer/composite technology area have dropped out again. Such departures from the scene of advanced structural ceramics have been a worldwide phenomenon during the last two years. The companies that still are active in this area now are much fewer in number and the future of the field is in their hands. In the United States, the Dow Corning Corporation is the major player remaining and this company has developed very promising polymeric precursors for silicon carbide and silicon nitride fibers and parts.

A hopeful sign is that government research agencies worldwide appear to recognize that the preceramic polymer/advanced ceramics technology is a vital one that is needed in continuing development of defense and aerospace programs in the twenty-first century, and that will be applicable also in other sectors such as transportation and energy. In the USA, various government agencies, including DOD, DOE, NASA and NSF, are sponsoring new R&D initiatives of various kinds in the advanced structural materials area, and are trying to involve academic, industrial, and the national laboratories in collaborative research, development and

even manufacturing programs. It is of particular importance to seek and recognize opportunities in the non-defense, non-aerospace market, but to penetrate that market will require imagination and ingenuity, as well as further technical advances.

In these discussions, I have focused on the *chemistry* of preceramic polymers. The success of a preceramic polymer will be measured by its utility in the production of useful materials – ceramics in most cases, but other materials as well (e.g., strengthened metal parts in the case of ceramic fiber-reinforced metal matrix composites). If the field of preceramic polymer chemistry is to flourish, “good” chemistry must be followed by “good” ceramics and “good” ceramics must ultimately give a “good” final product. To make this happen, the chemist must interact and collaborate with the ceramist/materials scientist and both must interact with the engineers of the end-use industry. Preceramic polymer chemistry presents interesting chemical challenges to the synthetic chemist and, because of these essential interactions with materials scientists and engineers, considerably widens his horizons. It has, I think, great potential for the future.

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